

TEMPERATURE EFFECTS DURING CAPILLARY RHEOMETRY TESTING

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Abstract

A non-contact temperature monitoring technique based on fluorescence spectroscopy was used to measure the temperature of a polymer resin during capillary rheometry testing. Polyethylene and polycarbonate doped with a fluorescent dye, perylene, were used in experiments to measure resin temperature changes due to shear heating as shear rate in the capillary increased from 10 s^{-1} to 10000 s^{-1} . Resin temperature at the exit orifice of a 1 mm diameter capillary die was found to increase monotonically with increasing shear rate reaching as much as $40 \text{ }^\circ\text{C}$ above the capillary set point temperature at the highest shear rates. The implications regarding rheometry testing are discussed.

Introduction

Rheometry experiments must be carried out under carefully controlled conditions of temperature and pressure, i. e. these parameters need to be measured accurately in order that the experiment be fully defined and controlled. In capillary rheometry, readily available pressure transducers yield accurate pressure measurements. But, the situation for temperature measurements is problematic. This is because commercially available temperature measurement methods, using either thermocouples or infrared radiometers, do not yield accurate resin temperatures. It is well known that experimental difficulties are experienced with both methods. For example, when a thermocouple probe is positioned in the wall of a capillary die, the capillary temperature dominates its response because heat transfer from the capillary to the thermocouple junction is much more efficient than heat transfer from resin to thermocouple. Inserting the thermocouple in the flow stream at the exit orifice is not advisable because thermocouple wires will conduct heat away from the material. IR radiometry can yield accurate resin temperatures for transparent resins of known emissivity, but emissivity is difficult to measure and changes value for each resin.

It has long been understood that, in capillary rheometry testing, energy is dissipated in the form of heat due the shear heating and compression heating and cooling.[1, 2] Since the objective of capillary rheometry is to report viscosity versus shear rate data at a constant temperature, a true resin temperature must be measured. It can not be assumed that the resin has the same temperature as the capillary die. Failing to account for the temperature rise due to viscosity introduces a source of error into the measurement. This effect has, until now, been neglected because of the difficulty of measuring the resin temperature.

To address the temperature measurement problem during capillary rheometry testing, we have developed a non-contact thermometry method based on fluorescence spectroscopy.[3] This paper presents results of temperature monitoring using the fluorescence technique for rheometer testing of polyethylene and polycarbonate.

Experimental Procedure

The method uses a temperature sensitive fluorescent dye that is doped into the resin. A dye mass fraction on the order of 10^{-6} of dye in the resin is sufficient for using fluorescence spectra as a monitoring tool. When mixed with the resin at elevated temperatures, the dyes are soluble in the resin matrix so that the dye is completely surrounded by the resin at the molecular level and does not tend to migrant or aggregate. The concept regarding fluorescent dyes is that they are molecular probes, i.e. they respond to their molecular environment and report conditions of the environment via their spectra. Thus, a fluorescence temperature is a true temperature of molecular origins.

Perylene, obtained from Aldrich Chemical Co., is the fluorescent dye used here.[4] Its excitation wavelength is 410 nm and its fluorescence is seen from 430 nm to 530 nm. In experiments with polycarbonate, we have used perylene up

to 300 °C without observing degradation[3]. Mixing with polyethylene, DOW Chemical 640, is achieved by first dissolving the dye in solution, pouring this solution over 5% of the to-be-processed resin pellets and evaporating the solvent which leaves behind pellets coated with dye.[4] The coated pellets were then mixed with the 95% uncoated pellets. The entire batch is then processed through an extrusion machine during which the pellets are brought to the melt state and blended together mixing the dye throughout the batch. After extrusion the batch is then repelletized. For mixing with polycarbonate, DOW 200, the dye and resin were combined using a common solvent, dichloroethylene, removing the solvent by evaporation, and extruding and pelletizing the material. This process does not yield entirely uniform concentration of dye throughout the batch, but in our measurements such variations cancel out because the results are expressed as ratios of fluorescent light intensity.

The primary modules of the optical measurement apparatus are: a xenon arc lamp light source, a bifurcated optical fiber cable, an optical sensor head with confocal optics design, a filtered beamsplitter for separating the spectra into different wavelength regimes, photomultiplier tubes (PMT) for light detection, and a Stanford Research SR 400 photon counter.[4] The basic optical setup is shown in Figure 1. For perylene, the two legs of the beamsplitter are filtered at 464 nm and 473 nm using bandpass filters with 5 nm bandwidth.

The measurement of temperature using fluorescence is based on changes that occur in the dye's spectrum as a function of temperature. For perylene, temperature induced changes are due to changes in the ground state and excited state energy levels and to transition probabilities of decay to different energy levels in the ground state. Consider the spectra for perylene shown in Figure 2. Distinct bands seen at 452 nm and 476 nm are associated with decay to different energy levels in the ground state. With increasing temperature, it is seen that the trough between the two bands loses definition. It is this shape factor that is used to correlate spectra and temperature. For the data of Figure 2, the standard uncertainty in the fluorescence intensity measurements is 0.5% and for temperature it is 1 °C.

The temperature measurement is based on changes in the ratio I_{464}/I_{473} . A typical calibration curve of I_{464}/I_{473} versus temperature for perylene doped polyethylene is shown in Figure 3. The standard uncertainty in temperature measurements using this calibration function is 2 °C.

A Goettfert 2003 servo-hydraulic capillary rheometer with capillary of 1 mm diameter by 30 mm long was used for these experiments.[4] Capillary temperature was controlled at 200 °C for polyethylene and 270 °C for polycarbonate. A pressure transducer for calculating the pressure drop is positioned above the entrance to the capillary. Figure 4

shows the experimental setup for interfacing with the optical sensor. The optical fiber is positioned to interrogate the resin flow stream at the exit of the capillary. The sensing tip is in the shape of a long rod with outer diameter of 6.35 mm (0.25 inch). It contains a small lens at its end with 6 mm focal length that focuses the excitation light onto the extruded strand of resin. The optical fiber cable contains a bundle of 19 fibers with 200 μm core, 6 of which transmit excitation light and the other 13 collect and transmit fluorescence to the beamsplitter.

The optical sensor is attached to a micrometer driven xyz translation stage that permits accurate positioning of the point of focus. In the experiments, we positioned the focus at three points: at the exit orifice, 0.5 cm beyond the orifice, and 1 cm beyond the orifice. The rationale for choosing these positions is that the measurements are taken through the spatial extent of the extrudate die swell.

The experimental protocol consists of loading a quantity of material in the rheometer reservoir, waiting ten minutes for the resin to achieve temperature equilibrium, applying pressure to the plunger in steps that generate a series of shear rates in the order: 100 s^{-1} , 10 s^{-1} , 20 s^{-1} , 50 s^{-1} ... increasing in 2, 5, 10 steps until the reservoir is empty. Fluorescence temperature measurements were made by integrating photon counts from the two PMTs over 0.5 s and storing the ratio in a data file. Measurements were made at intervals of 1 s.

In data plots presented below, we show a thermal degradation threshold of polyethylene at 215 °C. This is the temperature at which significant quantity of volatile gases were driven from the resin. We have not determined that the polyethylene resin is degraded in molecular weight when taken above 215 °C, but we have observed that this resin is discolored if its thermal history included temperatures above 215 °C. The degradation temperature for polycarbonate in air is 300 °C.

Results and Discussion

Figure 5 shows the results for polyethylene with the excitation light focused at 0.5 cm downstream beyond the orifice. The plot contains two y axes, fluorescence temperature and pressure. The standard uncertainty of the temperature measurement is 2 °C and for pressure it is 0.07 MPa. These plots show the data as a function of time over the time extent of a rheometer run. The last data points were obtained when the resin in the reservoir was exhausted. The shear rate achieved at various pressure levels is noted as well as the degradation threshold temperature of 215 °C and the barrel set point at 200 °C. Temperature stability of the barrel was within 0.2 °C, with a measurement standard uncertainty of 0.5°C. The accuracy of the rheometer piston speed as specified by the manufacturer is within 1% which yields shear rate values with maximum standard uncertainty of 1%.

The data of Figure 5, show that significant increase in resin temperature begins at approximately 50 s^{-1} . With the focus positioned at 0.5 cm downstream, the resin temperature exceeds the degradation temperature for shear rates above 1000 s^{-1} and this was accompanied by a visual discoloration of the extruded resin. We observed similar results with the focus positioned at the orifice and at 1 cm downstream with temperature increases of approximately equal size. Thus, measuring inside or outside the die swell has no consequence on the magnitude of the effect. In Figure 6, we plot apparent viscosity versus shear rate and note that the data at low shear rate were obtained at $200 \text{ }^\circ\text{C}$, but at high shear rate the temperature had increased to $220 \text{ }^\circ\text{C}$.

For polycarbonate, the data are shown in Figures 7 and 8. The effect of shear heating begins at 500 s^{-1} , the same shear rate for which shear thinning effects are displayed in the viscosity plot of Figure 8. The suggestion is that shear heating and shear thinning effects are concurrent. This is a hypothesis that will require further study, but can not be tested until the viscosity data are properly corrected for temperature effects.

Two fundamental questions arise concerning the measurement method: what is the effect of pressure and what is the effect of shear on the fluorescence temperature measurement? The questions are appropriate because the calibration curve was obtained at quiescent conditions. There are three factors that support the veracity of the numbers presented here. First, the overall temperature effect was observed to be the same for positions that extend through the die swell region. Second, shark skin, which we observed for shear rates above 1000 s^{-1} , had no discernible effect on the observations. Third, fluorescence anisotropy measurements have shown that the isotropic orientation of the perylene dye in polyethylene is maintained from 0 s^{-1} to 250 s^{-1} . [5] This means that the perylene dye occupies

microscopic free volume regions in the resin and does not participate in the macromolecular entanglement dynamics of the polymer as it undergoes shear flow. At the higher shear rates the perylene molecule maintains the same isotropic orientation distribution as for the quiescent state. Thus, the calibration curve of Figure 3 applies at high shear rates.

Viscosity versus shear rate functions at constant temperature are normally the output from capillary rheometry tests. But, these measurements demonstrate that the values obtained at high shear rates must be corrected for the temperature increase. The correction scheme will involve the development of temperature shift factors to correct the data.

Finally, it must be mentioned that the degradation observed in this test has thermal origins and is not the result of shear stresses. The degradation brings to our attention another effect that must be considered in the analysis of this data.

References

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2. C. Hieber, *Rheologica Acta* 16:553 (1977).
3. A. J. Bur, M. G. Vangel and S. Roth, *Polym. Eng. Sci.* 41, 1380 (2001).
4. Identification of a commercial product is made only to facilitate experimental reproducibility and to describe adequately the experimental procedure. In no case does it imply endorsement by NIST or that it is necessarily the best product for the experiment.
5. A. J. Bur, S. C. Roth and C. L. Thomas, *Rev. Sci. Instrum.* 71, 1516 (2000).

Keywords: capillary rheometry, optical sensor, fluorescence spectroscopy, shear heating, temperature, extrusion.

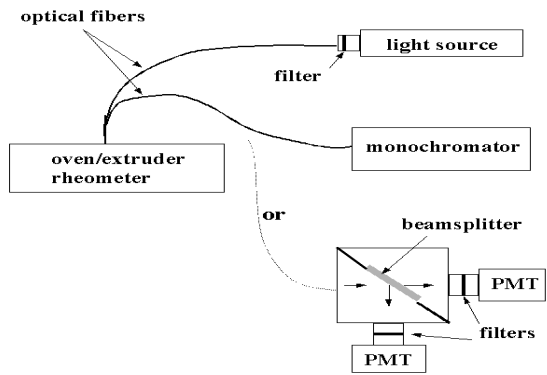


Figure 1. The general setup for fluorescence measurements is shown. For the data of Figure 2 the monochromator is used. For the data of Figures 3 and 5 the beamsplitter detector arrangement is used with PMTs filtered at 464 nm and 473 nm.

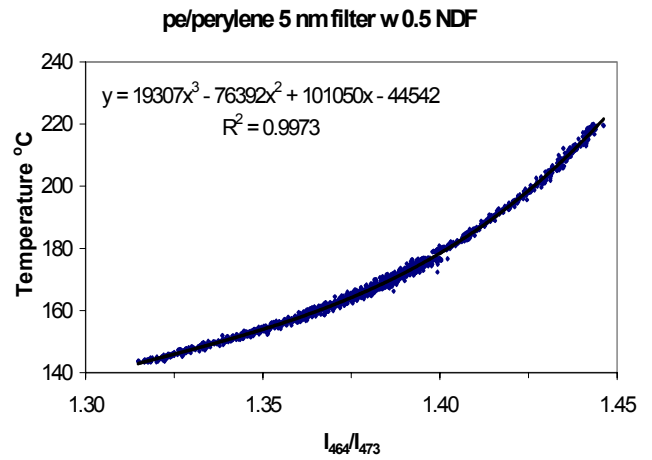


Figure 3. The calibration used for obtaining the data of Figure 5 is shown. The ratio I_{464}/I_{473} is larger than 1 because the beamsplitter/PMT arrangement yields ratios that depend on bandpass filter transmission and on PMT amplification factors.

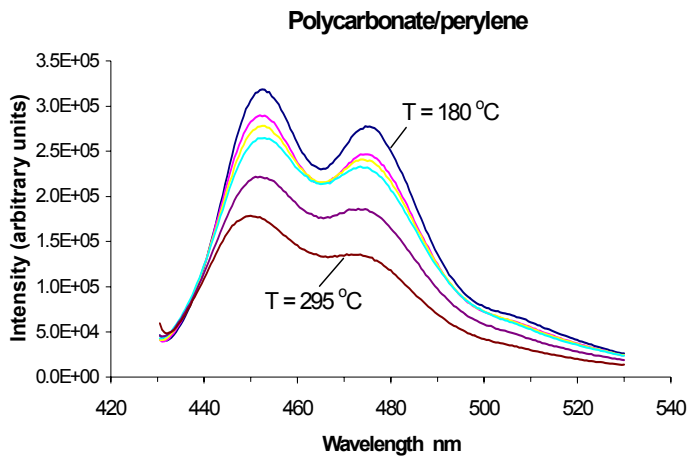


Figure 2. Fluorescence intensity of polycarbonate doped with perylene is plotted versus wavelength for temperatures between 180 °C and 295 °C. The data demonstrate how the spectrum of perylene changes with temperature. The ratio of intensity at the trough (464 nm) to that of the peak (473 nm) versus temperature yields a calibration curve similar to that of Figure 3.

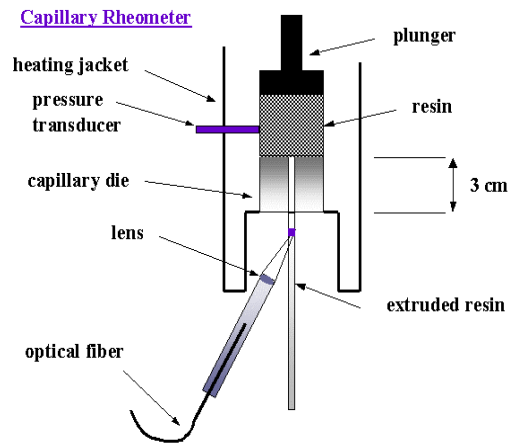


Figure 4. The experimental setup with capillary rheometer and optical sensor is shown.

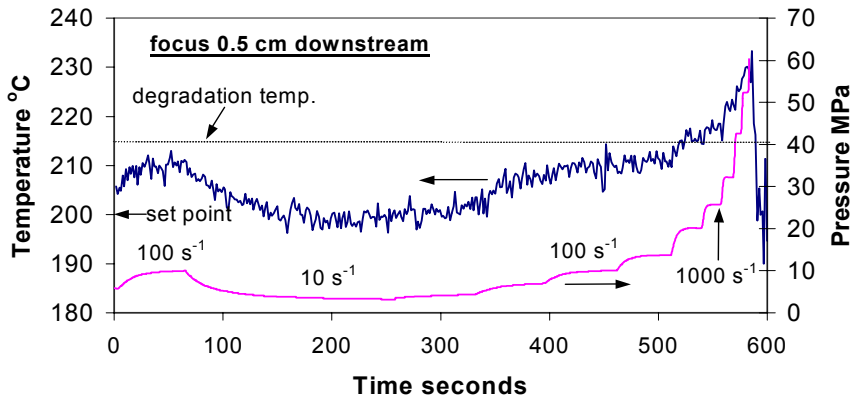


Figure 5. Capillary rheometer data for polyethylene.

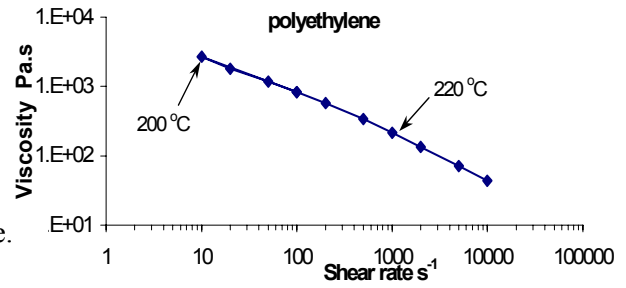


Figure 6. Viscosity versus shear rate for polyethylene.

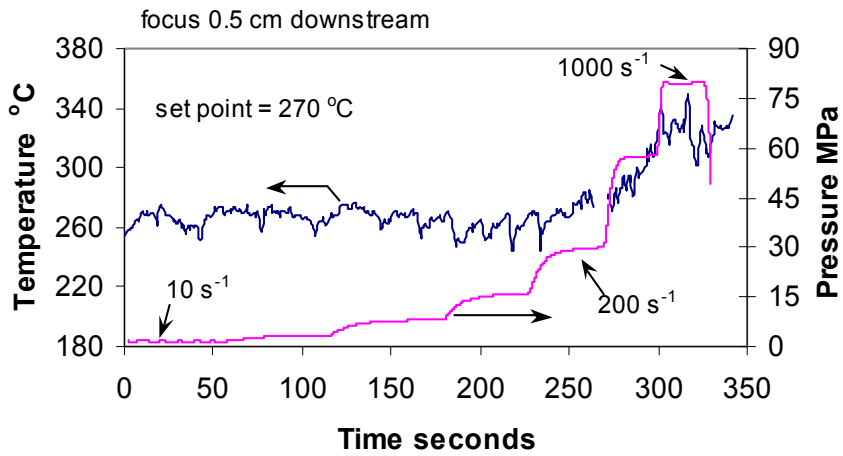


Figure 7. Capillary rheometer data for polycarbonate.

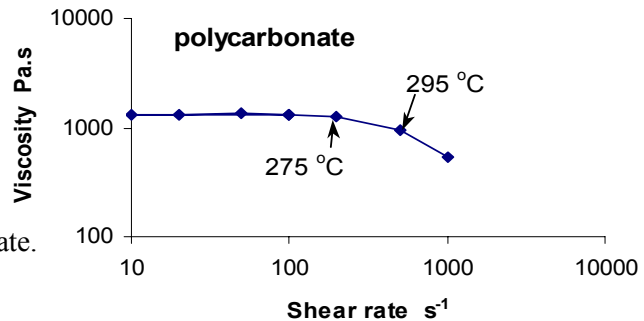


Figure 8. Viscosity versus shear rate for polycarbonate.